PRODUCT BULLETIN

LUCIDOL PENNWALT
CHEMICALS ■ EQUIPMENT
HEALTH PRODUCTS
1740 Military Road/Buffalo, New York 14240/716-877-1740

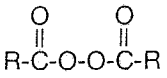
DPM 712 Luperco ATC

DIACYL PEROXIDES

INTRODUCTION

Diacyl peroxides are free-radical initiators which can be decomposed to useful free-radicals when heated or when activated by various promoters. They are widely used as initiators for vinyl monomer polymerizations, as curing agents for unsaturated polyester resins, and as crosslinking agents for elastomers.

These peroxides have the following general structure:



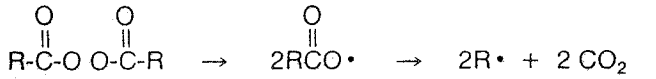
where R is an alkyl, cycloalkyl, aralkyl, aryl or heterocyclic radicals. Many diacyl peroxides are described in the literature, "Peroxides and Peroxy Compounds, Organic," Orville L. Mageli and Chester S. Sheppard, Encyclopedia of Chemical Technology, Volume 14, 1967.

COMMERCIAL PRODUCTS

The Lucidol Division of Pennwalt Corporation offers seven commercial diacyl peroxide formulations. The information relating to physical properties, thermal stabilities, and product packaging and handling of these formulations is given in Tables I-VI of this bulletin. Lucidol is capable of producing other formulations which satisfy customer requirements.

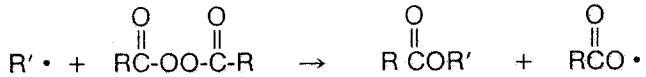
REACTIONS OF DIACYL PEROXIDES

A. *Thermolysis* — Thermal decomposition of diacyl peroxides results in production of commercially useful free-radicals by means of homolytic cleavage:



In dilute solution the rate determining reaction (Homolytic Cleavage) follows first order kinetics, therefore, half-lives at various temperatures can be calculated from the kinetic data. The reactivities of various diacyl peroxides can be rated by comparing the temperature at which the half-lives are one hour and ten hours. The 1 hour and 10 hour half-life temperatures for the commercial diacyl peroxides are given in Table VI. Other relative temperature/half-life relationships are given in Figure[1].

B. *Induced Decomposition* — In one type of induced decomposition reaction the oxygen-oxygen bond of the diacyl peroxide is attacked by an alkyl radical. This produces an ester and an acyloxy radical:

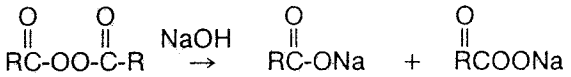


Induced decompositions should be avoided because they are inefficient free-radical generators. No net increase in free-radicals is obtained by this type of decomposition.

C. *Heterolytic Decomposition* — Intramolecular rearrangement (e.g., Carboxyl Inversion) of certain diacyl peroxides occurs when strong acids or polar solvents are present:

This reaction, like induced decomposition, results in no net increase in free-radicals.

D. *Hydrolysis* — Diacyl peroxides react with inorganic bases (e.g., NaOH) to form the salts of acids and peroxyacids:



HALF-LIFE DATA

The half-life of a peroxide at any specified temperature is the time required at that temperature, to affect a loss of one half of the peroxide's active oxygen content. Because the efficiency of a free radical initiator depends heavily upon its rate of decomposition, half-life data can be a useful guide in selecting the optimum initiator for a specific application.

Several factors must be kept in mind when using half-life data obtained in dilute solution, the first is that it only applies to thermolytic decomposition and the second is that half-life can vary in different solvents due to induced decomposition if no radical scavenger is present. In the presence of monomer, induced decomposition becomes relatively insignificant, and first order kinetics are observed in most cases. The published half-life data is only an approximation of observed polymerization kinetics, and serves as a relative comparison between initiators in similar systems.

Figure I is a composite representation showing half-life versus temperature of dilute solutions of several commercially available diacyl peroxides in common solvents. Table VI lists these products along with values for activation energy and temperatures calculated to produce one and ten hour half-life values in the given solvents.

APPLICATIONS

Free radicals generated by thermolysis are useful for unsaturated polyester resins and for crosslinking of elastomers.

Diacyl peroxides such as benzoyl peroxide can be promoted to achieve room temperature cures of unsaturated polyester resins and room temperature polymerization of acrylates. Tertiary amines such as dimethyl aniline are normally employed as promoters.

HANDLING AND STORAGE

Facilities — Diacyl peroxides should be stored apart from other non-peroxide chemicals, preferably in an isolated location. Buildings should be well ventilated. Freezer chests or walk-in refrigerators should be used to store the less stable diacyl peroxides. Containers of diacyl peroxides should be stacked so as to allow good air circulation.

Storage Temperatures — Diacyl peroxides are quite stable at or below their recommended storage temperatures. At higher temperatures decompositions can occur. Except for acetyl peroxide, frozen diacyl peroxides can be thawed at a temperature which is below the maximum storage temperature. Owing to the shock sensitivity of acetyl peroxide its formulations should not be allowed to freeze since shock sensitive crystals of pure acetyl peroxide can form. Simjlarly, due to the shock sensitivity of dry Succinic Acid Peroxide the 40% water formulation of this product should not be allowed to thaw creating higher peroxide concentrations by separation.

Shelf-Life — Except for paste formulations, properly stored diacyl peroxides have a shelf-life of at least one year. Paste formulations have a shelf-life of approximately six months when stored between 35°F and 85°F and approximately three months when stored between 85°F and 100°F. Paste formulations of solid diacyl peroxides have reduced shelf-lives owing to slight physical separations which occurs during storage and to somewhat lower thermal stability. These formulations should be thoroughly mixed in order to insure uniformity prior to use.

Containers of diacyl peroxide formulations should be dated when received and used or disposed of before the shelf-life period is exceeded.

HANDLING PRECAUTIONS

Heat — If a diacyl peroxide is heated above a certain temperature, its rate of decomposition increases in an uncontrolled manner. This reaction can be violent, releasing large volumes of hot, flammable gasses.

The temperature at which this occurs depends on the volume of diacyl peroxide, the container, and the period of time the diacyl peroxide remains at that temperature. The Self-Accelerating Decomposition Temperature (SADT) Test provides a measure of this hazard. The SADT temperature for each diacyl peroxide formulation in its largest shipping container is given in Table I.

Shock and Friction — Dry benzoyl peroxide (Lucidol 98) and dry Succinic Acid Peroxide are shock and friction sensitive. Crystallized acetyl peroxide is also shock sensitive. Commercial diacyl peroxides (except Lucidol 98) are formulated to be non-shock or friction sensitive and are very safe if handled and stored properly.

Fire — Diacyl peroxides burn vigorously and are difficult to extinguish. The usual precautions for flammable solids should be observed. If a small fire occurs, Class B extinguishers (dry chemical, foam or carbon dioxide) can be used. In case of a fire involving large quantities of diacyl peroxides, the area should be evacuated and the fire fought with water.

Contamination — Various contaminants, particularly oxidizing and reducing agents, metal salts and amines, can cause decomposition of diacyl peroxides.

Eye and Skin Irritation — Goggles or a face mask and gloves should be worn when handling diacyl peroxides. In case of skin contact, wash with soap and water. In case of eye contact, flush with water for at least 15 minutes and get medical attention.

Spillage — If a diacyl peroxide is spilled, vermiculite (or other, inert absorbent material) should be used to soak up liquids or mix with solids. When dry benzoyl peroxide or succinic acid peroxide is involved, the mixture should be wetted with water before sweeping up. The sweepings can be disposed of by scattering or burial in a remote area away from combustable materials, or they may be burned by controlled methods.

DISPOSAL

Dilution and Incineration — Dilution and Incineration is quickly becoming the most preferred method of liquid peroxide disposal due to current environmental regulations. Dilution of peroxide to less than 1% active oxygen or less than 5% by weight in a satisfactory solvent is recommended. Fuel Oil #2 or common hydrocarbons are the most widely used. Incineration can be accomplished after satisfactory mixing with negligible heat contribution from the peroxide portion of the solution. This method is not generally accepted for disposal of solid peroxides.

Disposal Companies — Disposal companies also may present one of the most desired ways of eliminating waste organic peroxides. In most cases dilution as described in the *Dilution and Incineration* section is required. Contact, however, should be made with the individual disposal company to guarantee first, acceptance of peroxides and second, their specific procedures.

Burning — Burning is the fastest and most efficient method of peroxide disposal. Burning should be carried out in remote areas and volumes should be limited to one gallon quantities of liquid peroxides or one pound increments of solid peroxides. The peroxides should be distributed uniformly and ignited with a long-handled torch.

Burial — Burial is an accepted method of small quantity disposal. Care should be taken in selection of a burial location where liquid leaching will not affect water sources such as wells and streams. Also the burial of benzoyl peroxide 98, succinic acid peroxide or acetyl peroxide in an excavation area is not recommended due to their shock sensitivity.

Hydrolysis — Hydrolysis is another effective way of disposing of small quantities of benzoyl peroxide, less than 10 pounds. This involves the addition of benzoyl peroxide to cold (30-40°F) 10% sodium hydroxide (caustic) solution. This reaction requires adequate agitation and temperature control between 30-40°F. Small increments of benzoyl peroxide should be added up to a 10% loading in the caustic solution. This reaction converts benzoyl peroxide to relatively innocuous sodium benzoate which can be disposed of by normal means.

In any disposal situation when doubts or questions exist, contact with a Lucidol representative is recommended.

Toxicity — The toxicity of diacyl peroxides has not been fully determined. These materials should not be allowed to remain in contact with the skin and inhalation of vapors should be avoided. Toxicological data in the form of the *SPI Commercial Organic Peroxide Toxicological Data* report is available on request.

Availability — The more stable diacyl peroxides are warehoused nationwide for immediate shipment by common carrier. Those which must be shipped under refrigeration are stocked in Geneseo, New York and Crosby (Houston) Texas. Lucidol operates a fleet of trucks from each location to provide delivery service to most points in the United States and Canada, and to major ports and border crossings for export. Formulations of benzoyl peroxide are marketed nationwide by special distributors serving the reinforced plastics industry.

For addition technical information, for prices, for placing orders and for the location of the nearest distributor, contact the Sales Department:

Lucidol Division, Pennwalt Corporation
1740 Military Road, Buffalo, New York 14240
Phone: (716) 877-1740.

FOOD AND DRUG ADMINISTRATION STATUS

The following compounds are named in the Code of Federal Regulations concerning food additives:

Peroxide	*Applicable Paragraphs*
2, 4-dichlorobenzoyl peroxide	121.2562
benzoyl peroxide	121.2530, 121.2526, 121.2562, 121.2576
acetyl peroxide	121.2520, 121.2526
lauroyl peroxide	121.2520, 121.2526, 121.2576

Request Technical Service Bulletin #7 "Lucidol Products Meeting Food Additive Regulations" for complete information.

TECHNICAL INFORMATION

The diacyl peroxides are only one of the many classes of organic peroxides manufactured by Lucidol. Product bulletins are available covering:

Ketone Peroxides
Peroxydicarbonates
Peroxyesters
Dialkyl Peroxides
Alkyl Hydroperoxides
Organosulfonyl Peroxides
Peroxyketals

More detailed information on the use and handling of organic peroxides is contained in technical bulletins:

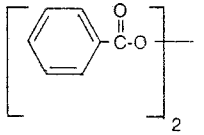
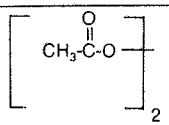
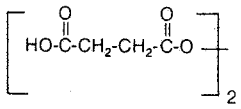
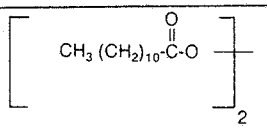
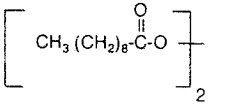
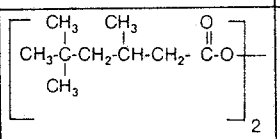
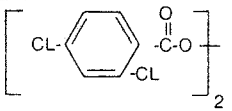
1. Bulletin 30.30 "Evaluation of Organic Peroxides From Half-Life Data"
2. Bulletin 30.43 "Safe Handling, Storage and Transportation of Peroxides Requiring Refrigeration"
3. Bulletin 30.40 "Organic Peroxides: Their Safe Handling and Use"
4. SPI Bulletin 19 "The Storage and Handling of Organic Peroxides in the Reinforced Polyester Fabricating Plant"
5. Bulletin 30.90 "Free Radical Initiators for the Suspension Polymerization of Vinyl Chloride"
6. Technical Data Bulletins "Selection of Free Radical Initiators for Curing Thermoset Resins"
   "Mixed Catalyst Systems for Increased Productivity in Mold Curing of Unsaturated Polyesters"
7. Technical Service Bulletin #7 "Lucidol Products Meeting Food Additive Regulations"
8. SPI Toxicological Data

The following safety films are also available:

"No Second Chance" "For Safety's Sake"
"The Safe Way Is The Only Way"
"Keep it cool . . . Keep it clean"

For literature, films, additional technical information or evaluation samples, contact the Marketing Services Department.

TABLE I PHYSICAL PROPERTIES

Peroxide Name	Peroxide Structure	Molecular Weight	Commercial Products	Form	Diluent	Melting/ Freezing Point F	Density @ °F g/ml Bulk Density lbs/ft³	Viscosity Cps @ C	Assay % by wt.	Active Oxygen % by wt.	Maximum Storage Temp. F	Maximum Storage Temp. C	S.A.D.T. F	S.A.D.T. C
BENZOYL		242	Lucidol-98	Granular	None	—	32.4 lbs/ft³	—	98.5±1	6.5±.07	100	38	155	68
			Lucidol-78	Granular	Water	<32° F.P.	39 lbs/ft³	—	75-80	4.95-5.28	100	38	155	68
			Lucidol-70*	Granular	Water	<32° F.P.	45 lbs/ft³	—	70±2	4.49-4.74	100	38	175	79
			Luperco AFR-500	Paste	Proprietary	<35° F.P.	1.19 @ 77°F	41 @ 25	50 min	3.3 min	100	38	—	—
			Luperco AFR-501	Paste	Proprietary	<35° F.P.	1.19 @ 77°F	41 @ 25	50 min	3.3 min	100	38	—	—
			Luperco ANS	Paste	Proprietary	<35° F.P.	1.22 @ 77°F	64 @ 25	55 min	3.6 min	100	38	125	52
			Luperco AFR-250	Paste	Proprietary	—	1.36 @ 77°F	8.8 @ 25	24-27	1.58-1.78	100	38	135	57
			Luperco ATC	Paste	Tricresyl Phosphate	<−30° F.P.	1.16 @ 77°F	24 @ 25	50-52	3.3-3.43	100	38	1(	43
			Luperco AST	Paste	Silicone Oil	<−30° F.P.	1.04 @ 77°F	—	50 min	3.3 min	100	38	145	63
			Luperco ACP	Powder	dicalcium phosphate	—	41.2 lbs/ft³	—	35-37	2.31-2.44	100	38	—	—
			Luperco AA	Powder	Wheat Starch	—	35 lbs/ft³	—	32-33	2.11-2.18	100	38	—	—
ACETYL		118	Acetyl Peroxide 25% solution	Liquid	dimethyl phthalate	17° F.P.	1.17 @ 77°F	7.6 @ 20	23-25	3.12-3.39	32-75	0-24	115	46
SUCCINIC ACID		234	Succinic Acid Peroxide	Frozen Solid	Water	257° M.P.	50 lbs/ft³	—	58-71	3.96 min	32	0	150	66
LAUROYL		399	Alperox-F	Flake	None	130° M.P.	.91 @ 77°F 27.6 lbs/ft³	—	98 min	3.93 min	80	27	120	49
DECANOYL		342	Decanox-F	Flake	None	104° M.P.	26 lbs/ft³	—	98.5 min	4.6 min	60	16	105	41
DIISONONANOYL		314	Lupersol 219 M75	Liquid	Odorless Mineral Spirits	−49° F.P.	.87 @ 50°F	32 @ −16	75-77	3.82-3.92	32	0	75	24
2,4 DICHLORO-BENZOYL		380	Luperco CST	Paste	Silicone Oil	<−30° F.P.	1.27 @ 77°F	380 @ 25	50 min	2.1 min	80	27	120	4(

*A U S P grade Lucidol-70S for use in pharmaceutical applications is also

TABLE II STANDARD PACKAGING CONTAINERS NET WEIGHTS AND VOLUMES

Peroxide	Commercial Products	1 lb. lined polyethylene Paper Bag	Polyethylene Bag	Fiberpak	1 lb. PE Jar	1 gallon PE Jug	5 Gallon HDPE Pail	Leverpak	Corr. Telescoping Carton	5 Gallon PE Deltangular	5 Gallon PE Cube	1 Gallon PE Bottle	Dot Shipping Classification
	Lucidol-98	25x1# 50x1#	—		—	—	—	—	—	—	—	—	Organic Peroxide
	Lucidol-78	—	25 x 1# 50 x 1# 2 x 10# 5 x 5#	1 x 25#	—	—	—	—	—	—	—	—	Organic Peroxide
	Lucidol-70	—	25 x 1# 50 x 1# 2 x 10# 3 x 10# 5 x 5#	1 x 25#	—	—	—	—	—	—	—	—	Organic Peroxide
BENZOYL	Luperco AFR-500	—	—	—	25 x 1#	4 x 8#	40#	—	—	—	—	—	None
	Luperco AFR-501	—	—	—	—	—	40#	580# (41 gal)	—	—	—	—	None
	Luperco ANS	—	—	—	25 x 1#	4 x 8#	40#	—	—	—	—	—	Organic Peroxide
	Luperco AFR-250	—	—	—	—	—	40#	320# (41 gal)	—	—	—	—	None
	Luperco ATC	—	—	—	25 x 1#	4 x 10#	40#	—	—	—	—	—	Organic Peroxide
	Luperco AST	—	—	—	25 x 1#	4 x 8#	40#	—	—	—	—	—	Organic Peroxide
	Luperco ACP	—	—	—	—	—	—	—	60#	—	—	—	None
	Luperco AA	—	—	—	—	—	—	100# (30 gal)	—	—	—	—	None
ACETYL	Acetyl Peroxide 25% solution	—	—	—	—	—	—	—	—	35#	—	—	Organic Peroxide
SUCCINIC ACID	Succinic Acid Peroxide	50x1#	—	—	—	—	—	—	—	—	—	—	Organic Peroxide
LAUROYL	Alperox-F	25x1# 50x1#	—	—	—	—	—	100# (30 gal)	50#	—	—	—	Organic Peroxide
DECANOYL	Decanox-F	—	—	—	—	—	—	50# (15 gal)	50#	—	—	—	Organic Peroxide
DIISONONANOYL	Lupersol 219 M75	—	—	—	—	—	—	—	—	—	35#	—	Organic Peroxide
2,4 DICHLORO-BENZOYL	Luperco CST	—	—	—	25 x 1#	4 x 8#	45#	—	—	—	—	—	Organic Peroxide

*Self accelerating decomposition temperature.

TABLE III OUTSIDE SHIPPING CONTAINER DIMENSIONS

Product Container	Outside Container	Approximate Carton Dimensions (inches)		
		length or diameter	width	height
25 x 1# PE Bags	Corrugated Carton	20 3/16	15 3/16	8 1/16
50 x 1# PE Bags	Corrugated Carton	20 1/8	15 13/16	14 7/8
25 x 1# PE lined paper bags	Corrugated Carton	20 3/16	15 13/16	8 1/16
50 x 1# PE lined paper bags	Corr. carton f/BPO*	20 1/4	16	13 1/2
	Corr. carton f/SAP**	20 1/4	16 3/8	15 3/4
Polyethlene bags 5 x 5#	Corr. carton	20 3/16	15 3/16	8 1/16
2 x 10# 1 x 25	Fiber Drum	11 1/2	—	16 1/2
PE Bag 2 x 25#	Corrugated Carton	20 1/8	15 13/16	14 7/8
	Fiber Drum	15 1/2	—	18 1/2
25 x 1# PE Jars	Corrugated Carton	19 5/16	19 1/4	5 1/16
PE Jugs 4 x 8# 4 x 10#	Corrugated Carton	15 11/16	15 11/16	7 5/8
5 Gallon HDPE Pail	None	12	—	14 1/2
41 Gallon Leverpak	None	22 1/4	—	27 1/4
30 gal Leverpak Luperco AA	None	16 1/2	—	27 3/4
30 gal Leverpak Alperox-F	None	17 1/2	—	33 3/4
15 Gallon Leverpak	None	16	—	21 1/4
Corrugated Carton Telescoping	None	20 1/8	15 13/16	14 7/8
5 Gallon Deltangular	None	10 1/4	10 1/4	15 1/2
5 Gallon Cubitaner	None	12	12	12 1/8

*Used only for Ludicol-98
**Used only for Succinic Acid Peroxide

TABLE IV SOLUBILITY DATA

Peroxide Name	Alcohols		Hydrocarbons						Chlorinated Hydrocarbons			Ester	Ketones		Ethers		Monomers			
	Methyl Alcohol	Ethyl Alcohol	Benzene	Cyclohexane	Hexane	Toluene	Xylene	odorless mineral spirits	Methylene Chloride	Chlorobenzene	Trichloroethylene	Ethyl Acetate	Acetone	Methyl Ethyl Ketone	Ethyl Ether	Tetrahydrofuran	Vinyl Acetate	methyl methacrylate	Styrene	Water
BENZOYL	SL	SL	S	SL	INS	MS	MS	INS	MS	MS	MS	MS	S	S	MS	S	MS	MS	MS	INS
ACETYL	CM	CM	CM	SL	MS	CM	CM	INS	CM	CM	CM	CM	CM	CM	CM	CM	CM	CM	CM	INS
SUCCINIC ACID	SL	MS	INS	INS	INS	INS	INS	INS	INS	INS	INS	INS	MS	SL	INS	S	INS	INS	INS	MS
LAUROYL	INS	INS	S	S	MS	S	S	SL	S	S	S	MS	MS	MS	S	S	MS	S	S	INS
DECANOYL	SL	SL	VS	VS	S	VS	VS	S	VS	VS	VS	VS	S	S	VS	VS	S	S	VS	INS
DIISON-ONANOYL	CM	—	—	—	—	CM	—	CM	CM	—	—	VM	CM	CM	—	—	—	—	—	—
2, 4 DICHLORO-BENZOY	SL	INS	S	SL	—	S	—	—	—	—	—	MS	MS	MS	MS	—	—	—	MS	INS

% by weight
@ 25°C

INS = Insoluble (<1)
SL = Slightly soluble (1-5)
MS = Moderately soluble (5-15)

S = Soluble (15-50)
VS = Very soluble (>50)
CM = completely miscible (100%)

TABLE V TYPICAL APPLICATIONS

Applications	Benzoyl Peroxides																
	Lucidol-98	Lucidol-78	Lucidol-70	Luperco AFR	Luperco ANS	Luperco AFR-250	Luperco ATC	Luperco AST	Luperco ACP	Luperco AA	Acetyl	Succinic Acid Peroxide	Alperox-F	Decanox-F	Lupersol 219 M75	Luperco CST	
POLYMERIZATIONS/CURING*																	
Acrylates	●	●	●	●	●	●	●				●	●	●	●			
Styrene	●	●	●											●			
Vinyl Chloride	●	●	●										●	●	●		
Polyester Resins*	●	●	●	●	●	●	●	●	●	●			●	●			
Vinylidene Chloride	●	●	●														
Vinyl Acetate	●	●	●														
Styrenated Alkyds	●	●	●	●	●	●	●	●	●	●			●	●	●		
CROSSLINKING																	
Silicone Rubber	●							●								●	
Rubber-maleic acid	●						●	●									
OTHERS																	
Pharmaceutical	●	●	●						●	●							
Flour										●							
Drying & Bleaching Oils	●	●	●										●	●			

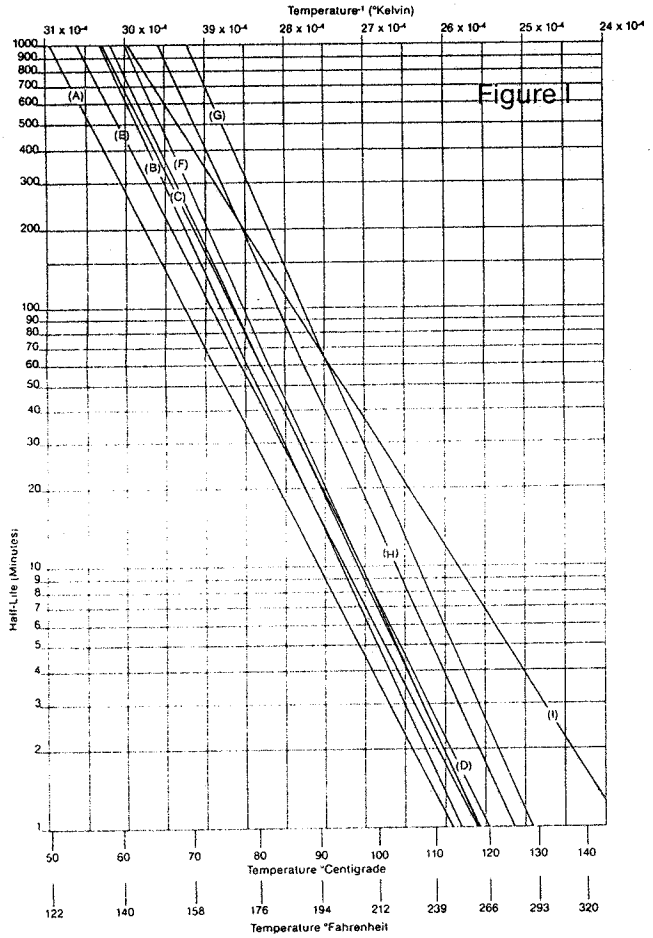


Figure I

TABLE VI

Product	Solvent	Concentration	E. Act. (Kcal/mole)	T ½ (°C) 10 hr.	T ½ (°C) 1 hr.
(A) Luperco CST	Benzene	.2m	28.0	54	73
(B) Lupersol 219 M75	Trichloroethylene	.2m	31.1	61	78
(C) Alperox-F	Benzene	.2m	30.5	62	80
(D) Decanox-F	Benzene	.2m	30.5	61	80
(E) Lupersol 219M 75	Benzene	.2m	29.7	58	77
(F) Alperox-F	Trichloroethylene	.2m	31.2	64	81
(G) Lucidol-98	Benzene	.2m	30.4	73	91
(H) Acetyl Peroxide	Benzene	.2m	26.0	69	87
(I) Succinic Acid Peroxide	Acetone	.1m	24.0	66	91

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